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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

KIM et al.

Serial No.: (Not Yet Assigned)

Filed: August 28, 2002

Atty. Docket No.: 02-419-US-PV

**SELF-ORGANIZED
NANOSTRUCTURES ON WAFERS
WITH CONTROLLED SYMMETRY AND
ORDER**

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60/407195
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Box Provisional Patent Application
Commissioner for Patents
Washington, D.C. 20231

PROVISIONAL APPLICATION COVER SHEET

Sir:

Transmitted herewith for filing under 37 C.F.R. § 1.53(b)(2) is the provisional application of:

INVENTOR(S)		
Given Name (first, middle)	Family Name or Surname	Residence (City and State or Country)
Hong Koo	KIM	PITTSBURGH, PENNSYLVANIA
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For: **SELF-ORGANIZED NANOSTRUCTURES ON WAFERS WITH CONTROLLED SYMMETRY AND ORDER**

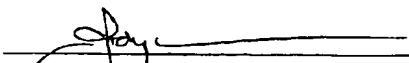
This application comprises of 29 pages of specification and drawings.

Enclosed are also:

- ☐ An assignment recordation cover sheet (in duplicate) and an assignment of the invention to [Assignee].
- ☒ Applicant claims small entity status under 37 CFR 1.9 and 37 CFR 1.27.

CERTIFICATE OF EXPRESS MAILING UNDER 37 C.F.R. §1.10

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Jody L. Burtner

Docket No.: 02-419-US-PV

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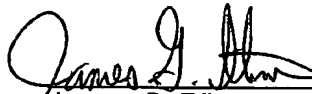
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SELF-ORGANIZED NANOSTRUCTURES ON WAFERS WITH CONTROLLED SYMMETRY AND ORDER

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

- [1] The present invention relates to methods for arranging highly-ordered nanopore arrays with controlled symmetry onto a foreign substrate surface. The present invention further relates to establishing a pattern over macro-scale areas of a substrate to promote the formation of nanopore arrays. The present invention also relates to the nanocircuitry and nanomachines that may be produced from such ordered arrays on a substrate.

2. DESCRIPTION OF THE BACKGROUND

- [2] Silicon and silica are widely used for the construction of semiconductor and optical devices that are currently employed in a variety of industrial settings, including computers, optical routing devices, and fuel cells. As computational demands of semiconductor devices increase, there is increasing pressure on the semiconductor industry to reduce the size of semiconductor devices while maintaining or improving the functionality and

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speed of that circuitry. Accordingly, substantial efforts to manufacture and manipulate silicon and other substrates at the sub-micron level have been pursued. Ideally, such a process would be characterized by a low manufacturing cost and high device throughput to facilitate industrial application.

- [3] The sub-micron manipulation of a substrate is hindered by the minute dimensions of the processing. In order to perform manipulations at this scale, engineers attempt to take advantage of the inherent property of some atoms and molecules to self-organize into nanometer-scale arrays. A review of anodic oxidation of compounds to form nanoscale pores may be found in O'Sullivan and Wood, *Proc. Roy. Soc. Lon.* 317: 511-543. For example, electrochemical oxidation of elemental aluminum results in anodic alumina which is a nanoporous material that shows a tendency to form self-organized pore arrays of triangular symmetry. Each pore has a diameter of ranging from approximately 4 to approximately 200 nanometers. Nanopores of alumina are known to form at seed points that are generated at creases or indentations in the surface of a substrate.
- [4] The patterned, nanoporous alumina could be used in the generation of various nanoscale machines and circuits

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using skills commonly known in the art. However, the production of ordered arrays of nanoporous alumina or other materials over relatively large areas of substrate (e.g., approximately 1 cm²) is limited by several characteristics of the techniques that are currently employed to make nanoporous alumina using aluminum foil and alumina films.

[5] Aluminum foils are often used as both a source of elemental aluminum as well as a structure on which the alumina nanopores are formed. Alternatively, aluminum films may be deposited onto a substrate that would then structurally support the subsequent formation of alumina nanopores from the aluminum film.

[6] The use of aluminum foil for the formation of alumina pores is associated with several drawbacks. First, elemental aluminum is not a semiconductor material and, therefore, its use as a substrate limits its utility with respect to subsequent processing steps. In addition, seeding of the alumina nanopores occurs randomly across the face of the aluminum foil. Accordingly, the domain size (i.e. an area of nanopores that has the same triangular symmetry) that is generated on bulk aluminum foil is usually limited to a micrometer scale, thus reducing the utility of these materials for

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applications that require larger areas of uniform symmetry. Finally, aluminum foil is not very physically stable and this property further constricts the potential applications to which nanoporous aluminum or aluminum foil can be applied.

[7] Aluminum films that are approximately 1 micron thick may be deposited onto foreign substrates such as silicon and silica and may be oxidized to form nanoporous alumina arrays. The diversity of substrates onto which aluminum may be deposited offers much broader application than those on bulk aluminum foils. However, attempts to grow ordered pore arrays using aluminum films have historically been unsuccessful, because nanopores typically form at seed points that are randomly distributed across the aluminum film resulting in an amorphous arrangement of pores. Development of ordered domains is disrupted by the randomly-distributed, densely-spaced grain boundaries from the initial stage of pore formation. As such, the growth of ordered alumina pore arrays using aluminum films has remained as a major challenge for the material science field.

[8] Attempts to increase the size of ordered domains of alumina nanopores have employed numerous techniques, including nano-indentation, electron-beam lithography,

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focused ion-beam etching, and scanning-probe-based writing. All of the techniques involve altering the surface of the substrate (e.g., silicon or aluminum foil) so as to promote formation of larger domains of ordered alumina nanopores. Each of the processes possesses limitations that hinder its application to the generation of ordered domains in an industrially useful setting.

- [9] The first step in nano-indentation is the construction of a mold. A defined pattern is etched onto the surface of a rigid material, such as silicon carbide, using a lithographic technique, such as electron beam lithography. The etched mold is then pressed into the substrate (typically aluminum foil) using a high pressure system to stamp the pattern of the mold into the substrate. This pattern would then direct the later formation of alumina nanopores. One limitation of this process is the very high pressure that is required to impress the pattern into the substrate. For an industrially-relevant area, the force required is too big to be industrially feasible to stamp the substrate. In addition, the application of this technique is limited by the properties of the substrate that is stamped. For example, this technique may not be applied to aluminum films because the aluminum film is too thin

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(~1 micron) to be imprinted. Furthermore, a substrate such as silicon or silica may be too delicate to stamp with such high pressure techniques. Finally, the initial etching of the mold is a very laborious and low throughput procedure. Although a mold may be reused, changes in the pattern require a complete retooling of the stamp at a cost of great time and expense.

[10] The lithographic technique of focused ion beam etching may also be used to etch patterns into aluminum foils. These patterns would promote the formation of nanoporous alumina. However, this process is very time consuming and expensive to employ.

[11] Similarly, scanning probe-based techniques also suffer from being time consuming and expensive. Scanning probe techniques, such as atomic force microscopy and scanning tunneling microscopy, are often used for topographic surface analysis. However, the stylus that is employed in these processes may also be used as an electrode to pass current so as to etch the surface of the substrate. For large, industrially-relevant areas, this process is prohibitively time consuming and expensive.

[12] Because of these and other limitations of traditional techniques, the semiconductor industry has had a long standing need to produce ordered nano-structures onto

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arbitrary substrates. Particularly, current methods have been unable to accomplish this task in an efficient and cost effective manner. In addition, no currently known technique is able to produce ordered nanostructures across large (~ 1 centimeter) areas of a substrate.

SUMMARY OF THE INVENTION

- [13] In accordance with the present invention, there are provided systems and methods for the production of self-ordered nanostructures on wafers with controlled symmetry and order. The methods of the present invention may be employed to arrange ordered arrays of nanopores over large areas of an arbitrary substrate. The regular arrangement of nanopores allows for the small scale manipulation of substrate. Accordingly, utilizing the present invention and skills commonly known in the art, numerous nanoscale electronic, photonic, and chemical devices may be designed, engineered, and constructed.
- [14] In a presently preferred embodiment, a wafer of a substrate such as silicon or silica is initially coated with photoresist material. The technique of holographic lithography may then be employed to etch away the photoresist in a distinct pattern, resulting in

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a pattern of exposed corrugation across the surface of the substrate.

- [15] A material, such as aluminum, may then be deposited onto the corrugated surface in a thickness such that the corrugation pattern is maintained across the surface of the wafer. The deposited material should be chosen based on its ability to form nanoporous arrays. For example, upon anodic oxidation aluminum forms alumina nanopores. Upon anodic oxidation of the deposited aluminum, nanopores form across the face of the wafer. However, the nanopores form in the crevice of the corrugation pattern, and, therefore, the nanopores are arranged regularly across the entire face of the substrate wafer.

BRIEF DESCRIPTION OF THE DRAWINGS

- [16] For the present invention to be clearly understood and readily practiced, the present invention will be described in conjunction with the following figures, wherein like reference characters designate the same or similar elements, which figures are incorporated into and constitute a part of the specification, wherein:

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[17] **Figure 1** is a schematic of the apparatus used in performing holographic lithography;

[18] **Figure 2** shows to a scanning electron microscopic image of the cross-section of a 1D grating patterned substrate;

[19] **Figure 3** displays a presently-preferred embodiment wherein a square symmetry photoresist grating pattern is developed on a silica substrate;

[20] **Figure 4** depicts aluminum films with thickness of approximately 350-400 nanometers on a 1-D grating;

[21] **Figure 5A** is a scanning electron micrograph of square-lattice arrangement of square-shaped pores with square arrangement of pores observed across the entire grating area;

[22] **Figure 5B** shows a higher magnification of a square-lattice arrangement of square-shaped pores;

[23] **Figure 5C** depicts a cross-sectional image of alumina nanopores showing that the pores grow well aligned to the center of the corrugation bottoms; and

[24] **Figure 5D** is a scanning electron micrograph of alumina pores obtained from a triangular-lattice 2D-

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grating-patterned aluminum film that was deposited onto a silica substrate at low and high (inset) resolution.

DETAILED DESCRIPTION OF THE INVENTION

[25] It is to be understood that the figures and descriptions of the present invention have been simplified to illustrate elements that are relevant for a clear understanding of the invention, while eliminating, for purposes of clarity, other elements that may be well known. Those of ordinary skill in the art will recognize that other elements are desirable and/or required in order to implement the present invention. However, because such elements are well known in the art, and because they do not facilitate a better understanding of the present invention, a discussion of such elements is not provided herein. The detailed description will be provided hereinbelow with reference to the attached drawings.

[26] The present invention provides for the rapid and efficient production of symmetrical arrays of nanoporous structures across large areas of substrate. In a presently-preferred embodiment, the substrate is silicon or silica and the nanoporous material is anodic alumina. However, one of skill in the art will recognize that the methods and compositions described herein are applicable

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to a wide variety of substrates including, but not limited to, silicon, silica, gallium-arsenide, indium phosphide, gallium phosphide, and plastic. In addition, one of skill in the art would recognize that the methods and compositions described herein are applicable to a wide variety of substances that form nanoporous structures such as titanium oxide (Gong et al., (2001) J. Mat. Res., vol. 16(12), pp. 3331 - 3334), which is hereby incorporated by reference). In general, any metals or semiconductors that can be oxidized to form nanoporous structures may be employed in the context of the present invention.

- [27] Generally, the arrangement of pores (*i.e.* both the order and symmetry of pore arrays) can be well controlled and guided by nanoscale surface corrugations of aluminum films. The present invention preferably provides for a holographic lithography technique to be utilized in conjunction with a conformal film deposition process to generate corrugation patterns that form a lattice across macroscale area of aluminum film prior to anodization. The lattice may be in arbitrary shapes, with square and triangular lattices being two presently-preferred embodiments. The lattice provides a structured pattern for seed points for the formation of nanopores. The nanoscale corrugation of films thereby allows for the

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formation of highly ordered (defect-free, single-domain) pore arrays on macroscale area ($\sim\text{cm}^2$).

- [28] In accord with at least one presently-preferred embodiment of the present invention, an area of substrate is initially coated with photoresist. The coating of substrate with photoresist may occur by dipping, spraying, spin coating, or any other procedure than produces a smooth layer of photoresist with controllable and uniform thickness across the area of desired dimension. For example, the photoresist may be coated as a 100-150 nanometer layer onto a silica substrate. The photoresist is then etched using the technique of holographic lithography. To perform holographic lithography, a laser beam is split into two beams. The two beams are then reflected so that they converge together onto the area of the photoresist-coated substrate. Where the two beams converge, an interference pattern comprised of multiple parallel lines of intense light is generated. The parallel lines of intense light occur with a particular periodicity which may be adjusted by changing the incident beam angle. Further adjustment of the periodicity may be accomplished by changes in optics, e.g., light source. Thus, the photoresist is etched away from the substrate beneath the interference pattern, thereby revealing .

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lines of exposed substrate. Such a patterning is preferably referred to as a one-dimensional or 1D pattern.

[29] As shown in **FIG. 1**, in a presently-preferred embodiment, a helium-cadmium laser (325 nanometer wavelength, 15 milliwatt output power) beam is expanded and collimated into a beam diameter of one to two centimeters and then split into two equal intensity beams. The two beams are then preferably recombined onto a photoresist (SHIPLEY 1805 positive photoresist diluted with thinner P solution in 1:1 volume ratio)-coated silica substrate to form the interference pattern. The grating pattern size is scalable to larger values with appropriate changes in the optics.

[30] Preferably the exposure intensity and exposure time are adjusted such that the substrate surface is fully revealed for approximately half of the grating period. **FIG. 2** displays a scanning electron microscopic image of the cross-section of a 1D grating patterned substrate. The corrugation depth of the photoresist grating in this example is approximately 120 nanometers.

[31] In a presently-preferred embodiment, the photoresist-coated substrate is double or triple exposed to the incident laser light with 60 or 90 degrees of rotation

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between the exposures for triangular or square symmetry, respectively. FIG. 3 displays a presently-preferred embodiment wherein a square symmetry photoresist grating pattern is developed on a silica substrate. Thus, the etched pattern displayed is essentially the summation of the two interference patterns. Additional etched patterns may be generated by changing the angle of rotation or the number of exposures. In the case of more than one exposure, each exposure pattern can be designed to be different in terms of the grating period and geometry (e.g., linear or curved).

- [32] In the next step of the process, the compound that is to form the nanoporous structures is preferably deposited onto the photoresist-patterned substrates. Deposition may occur by vacuum evaporation, such as thermal or electron beam evaporation techniques. In this embodiment of the present invention, the material to be deposited is evaporated in a high vacuum (typically 10^{-6} Torr or lower pressure), so that the mean-free-collision-path of evaporated particles is larger than the distance from the source to the substrate. These conditions would result in a deposition of evaporated material on substrate, producing conformal profiles of films deposited on a corrugated surface.

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[33] FIG. 4 displays a presently-preferred embodiment in which aluminum has been deposited onto a 1-D photoresist-patterned substrate. In the presently-preferred embodiment displayed in FIG. 4 aluminum films with thickness of 350-400 nanometers were deposited onto the 1-D photoresist-patterned substrate using a thermal evaporation method with a 99.999% purity aluminum source. The deposited film surface preferably conforms to the corrugation profile of the photoresist-patterned substrate with nearly the same amount of corrugation depth, that is, approximately 100 nanometers.

[34] Anodic oxidation of the deposited film is then preferably carried out. In a presently-preferred embodiment, an aluminum film that has been deposited onto a silica substrate is anodically oxidized in dilute electrolyte (1 H_3PO_4 + 800 H_2O in volume ratio) at room temperature using a platinum wire as a counter electrode. The anodization is preferably conducted under a constant voltage mode for 40 minutes. The anodic voltage is chosen such that the expected pore distance matches the grating period, for example 140 volts for a 350 nanometer grating period. In a naturally-formed alumina pore array, the interpore distance is known to be proportional to the anodization voltage, i.e. ~ 2.5 nanometers/volt. After anodization,

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the samples are preferably treated with phosphoric acid (diluted with water in a 1:3 volume ratio) for one to two minutes.

[35] FIG. 5A displays a low resolution scanning electron micrograph of a square-lattice arrangement of square-shaped pores with square arrangement that were formed by oxidation of deposited aluminum. The arrangement of pores across the entire surface is extremely regular, corresponding to the etched photoresist. FIG. 5B is a higher resolution image of square-shaped pores. FIG. 5C shows a cross-sectional view of alumina nanopores formed using a 1-D etching pattern. FIG. 5D displays an embodiment of the present invention where the photoresist-coated substrate was exposed to two diffraction patterns that were rotated 60 degrees with respect to one another. The resulting triangular arrangement of alumina pores is displayed at both high and low magnification.

[36] The embodiment described above involves substrate patterning prior to film deposition. An alternative process may also be employed to generate surface corrugation on deposited films. Initially, aluminum films may be deposited onto unpatterned substrate. Subsequently, photoresist grating patterns may be placed

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onto the deposited films. The grating pattern may then be transferred onto the aluminum film using a commonly-known etching technique, such as chemical or dry etching. A thin film may be introduced between aluminum film and photoresist in order to enhance the maximum etch depth in the pattern-transfer etching process. Following etching of the deposited aluminum, the remaining photoresist or etch mask is removed, revealing surface-corrugated aluminum films. Unlike the previously-described embodiment, this embodiment does not leave any photoresist remaining on the substrate.

[37] The resulting alumina pores typically show uniform depth (400 nanometers) and the pore bottom has a concave, hemispherical shape with barrier thickness of approximately 300 nanometers. The pores typically grow well aligned to the center of the corrugation bottom region. This result suggests that the nanoscale periodic corrugation of aluminum film surface can fully compensate for the randomizing effect of grain boundaries typically observed in aluminum films.

[38] The large areas of substrate that possess ordered arrays of nanoporous alumina have a variety of industrial applications that are contemplated within the scope of the present invention. These applications include, but

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are not limited to microelectronics, the construction of optical nanodevices, fuel cells, nano-structuring, and chemical catalyst applications.

- [39] Placing ordered arrays of nanoporous alumina onto a silicon wafer provides for several microelectronic applications. The alumina pattern may be used as a template for the later manipulation of the underlying silicon substrate. For example, the nanopores may be used to direct deep etching of the silicon wafer by techniques commonly employed in the art. Subsequently, a silicon oxide could be deposited into the wells produced by the deep etching along with an electrode so as to produce a folded capacitor. Such capacitors would be at a very high density across the face of the chip and could be used in a variety of applications commonly known in the microelectronics art. For example, a magnetic substance may be placed in pores that are etched into the silicon and ultra-high density storage devices could be produced. Alternatively, packing magnetic materials into the pores may be used to produce a high sensitivity magnetic sensor. Background for this topic may be found in Routkevitch et al., IEEE Trans. Electron Dev. 43 (10): 1646 (1996); Black et al., Appl. Phy. Lett. 79:409 (2001); Metzger et al., IEEE Trans. Magn. 36 (1):30 (2000).

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- [40] Placing an appropriately optically-active substance into pores (or in deeply etched holes generated using the pores as a mask) may also produce nano-machines that could be used to manipulate light. Optical fibers that are used industrially to transmit information via light require decoding and routing of that information. Currently, the routers that are employed are limited by the ability to bend the light beam while retaining all of the information contained within the beam. By packing an appropriate material into alumina nanopores and the surrounding material, an optical micro device called a photonic crystal may be produced. Photonic crystals have been shown to be highly effective in bending light beams relatively sharply, while retaining the information contained within the beam.
- [41] Such nanoporous arrays would be useful for the production of fuel cells. Using the alumina nanopores as a mask for deep etching, a large capacity physical storage media could be created. If the deeply-etched pores were filled with the appropriate materials, such as polytetrafluoroethylene, high voltages between wells could be generated and, as such, high capacity fuel cells could be manufactured. Background material on fuel cells may be found in Carrette et al., Fuel Cells, 1(1): 5-39 (2001).

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[42] Alumina nanopores generated according to the methods of the present invention could also be used to manufacture high resolution digital displays. By plating magnetic cobalt at the bottom of a deeply-etched pore and subsequently supplying ethylene gas and heat, a carbon nanotube may be formed along the pore. Because of the electron emissions that the carbon nanotubes create, such assemblies could be useful in the production of flat-panel displays. In addition, if the substrate on which the alumina nanopores were formed as plastic, flexible, high resolution displays could be produced. Structured nanopores could be used further as a guide or template for the ordering or stacking of not only carbon nanotubes, but of any material. Background on the use of carbon nanotubes may be found in Li et al., Appl. Phys. Lett. 75(3):367 (1999); Bae et al., Adv. Mat. 14(4):277 (2002); Choi et al., Appl. Phys. Lett. 79(22): 3696 (2001).

[43] Deep etching of a substrate using nanopore structures can also produce materials with high utility as a chemical catalyst. For example, titanium oxide also forms nanopores after oxidation of elemental titanium. Such nanopores have extremely large surface areas making them ideal for use as catalysts, particularly since the catalytic properties of titanium oxide are well known.

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Background on catalytic properties of titanium oxide may be found in Gong et al., Mat. Res. 16(12): 3331 (2001); Yamashita et al., Appl. Surf. Sci. 121/122:305 (1997).

[44] In a still further application, ordered nanoporous membranes may be obtained by introducing an additional intermediate layer of material between the nanoporous material and the substrate. The intermediate layer may be composed of a material that is able to be etched away using a chemical etching process. The procedure of obtaining ordered arrays of nanopores onto a substrate may proceed as described above. However, the nanoporous arrays would form on the surface of the intermediate layer. Following formation of the oxidized nanopores, the intermediate layer could be etched away, thus detaching the nanoporous array. The lower, closed portion of the pores could then be opened by chemical treatment. The resulting material would functionally operate as a very fine membrane. Such membranes would have utility in a variety of chemical and biochemical separations applications. Background on nanoporous filters may be found in Lee et al., Science; 296:2198 (2002).

[45] Although the invention has been described in terms of particular embodiments in an application, one of

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ordinary skill in the art, in light of the teachings herein, can generate additional embodiments and modifications without departing from the spirit of, or exceeding the scope of, the claimed invention. Accordingly, it is understood that the drawings and the descriptions herein are proffered only to facilitate comprehension of the invention and should not be construed to limit the scope thereof.

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While the following statements are phrased in the manner of claims of a utility patent application, they are not intended and should be hereafter construed to be claims. Accordingly, these statements should not be used for the purposes of prosecution history estoppel in any subsequent prosecution in which the statements bear resemblance to later filed claims. The following statements are intended only to point out particular aspects of the present invention for explanatory purposes.

Some aspects of the present invention include:

1. A method for arranging highly-ordered nanopore arrays with controlled symmetry onto a foreign substrate surface, comprising the steps of:

coating a substrate with photoresist;

photo-etching the photoresist to expose patterns comprised of said substrate;

depositing a material capable of forming nanopores onto said photoresist and said exposed substrate; and

anodically oxidizing said material to produce nanopores.

2. The method of Claim 1, wherein said photo-etching step is performed using holographic lithography.

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3. The method of Claim 1, wherein said pattern is selected from the group consisting of square and triangular.

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ABSTRACT

[46] Methods for arranging highly-ordered nanopore arrays with controlled symmetry onto a foreign substrate surface. The methods of the present invention may be employed to arrange ordered arrays of nanopores over large areas of an arbitrary substrate. Using holographic lithographic etching of photoresist, a regular pattern of corrugation may be generated on the surface of a wafer of substrate. A material, such as aluminum, may then be deposited onto the corrugated surface-in a thickness such that the corrugation pattern is maintained across the surface of the wafer. The material to be deposited should be able to form nanoporous arrays. For example, upon anodic oxidation aluminum is able to form alumina nanopores. By employing the methods of the present invention, nanopores typically form in the crevices of the corrugations. Accordingly, nanopores are arranged regularly across the entire face of the wafer. The regular arrangement of nanopores allows for the small scale manipulation of substrate. Accordingly, utilizing the present invention and skills commonly known in the art, numerous nanoscale electronic, photonic, and chemical devices may be designed, engineered, and constructed.

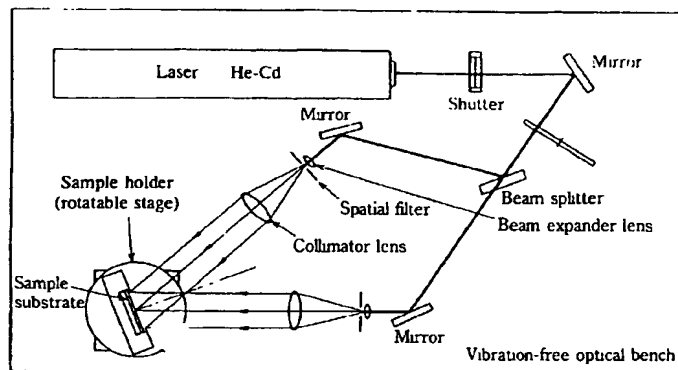


Figure 1

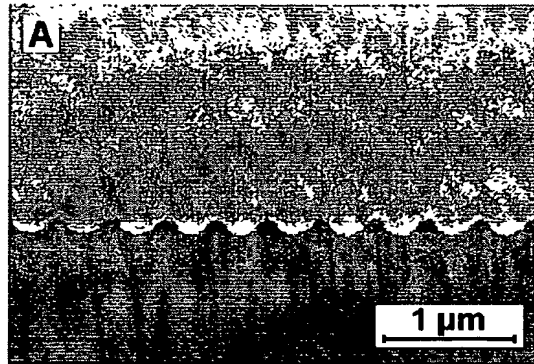


Figure 2

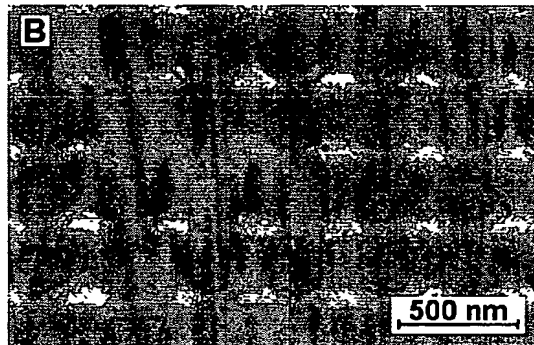


Figure 3



Figure 4

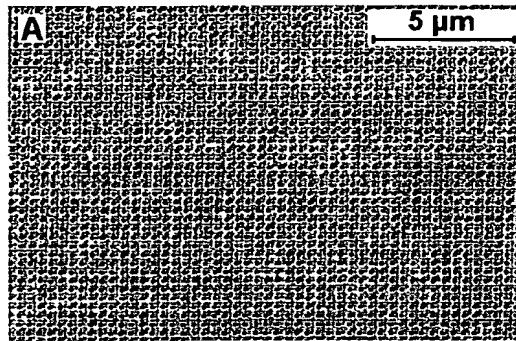


Figure 5(a)

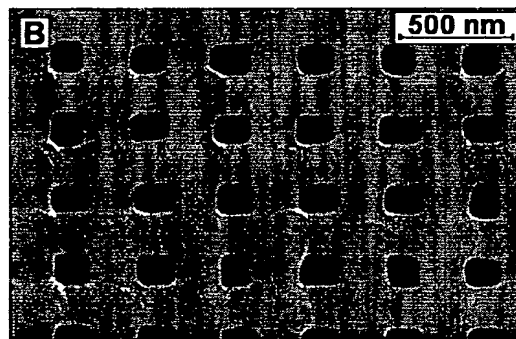


Figure 5(b)

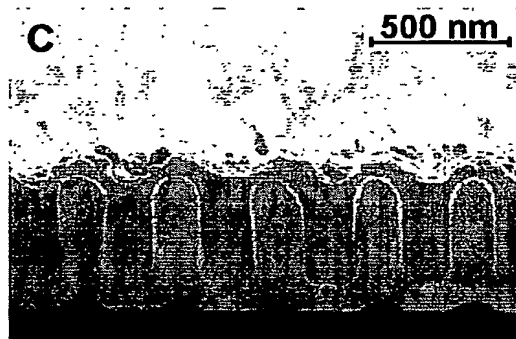


Figure 5(c)

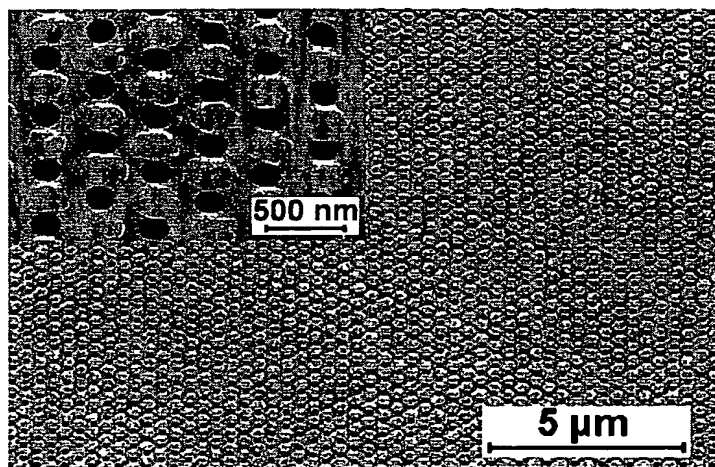
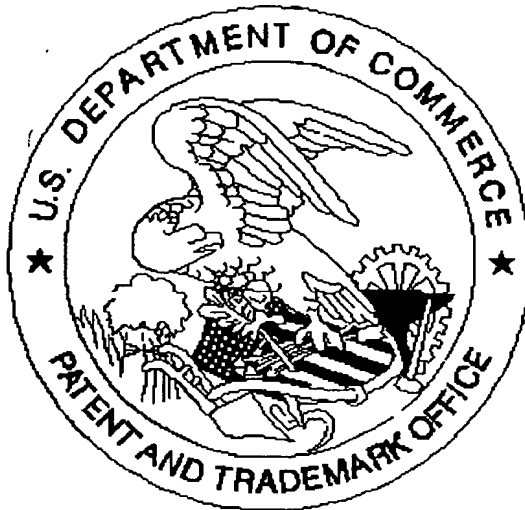


Figure 5(d)

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